

**PART 1 (To be returned to the invigilator)**

**DEPARTMENT OF CHEMISTRY, IIT MADRAS**

**CY 1001: Structure, Bonding and Reactivity (Module I-Physical Chemistry)**

**B. Tech. Mid Semester Examination; October 16, 2010**

**Marks: 75 (parts 1 & 2); Time: 1.5 hours**

---

**Important Note:** Answer questions from 1 to 18 (**Part 1**) in the space provided in the question paper itself and hand over this sheet of the question paper to the invigilator.

---

Boltzmann constant,  $k = 1.380658 \times 10^{-23} \text{ J K}^{-1}$ ; Gas constant,  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  
Planck constant,  $h = 6.626 \times 10^{-34} \text{ Js}$ ; Avogadro Number,  $N_A = 6.022 \times 10^{23}$

---

**Questions from 1 to 18 carry 1 mark each**

1. Assume that one mole of a gas in an isolated system is expanded to twice its original volume. The probability that all the molecules remain in the original space is \_\_\_\_\_.

(a)  $\left(\frac{1}{2}\right)^{6.022 \times 10^{23}}$     (b)  $(2)^{6.022 \times 10^{23}}$     (c)  $\left(\frac{1}{2}\right)$     (d)  $\frac{0.5}{6.022 \times 10^{23}}$     Ans.: a

2. At absolute zero, the entropy of  $\text{N}_2\text{O}$  is greater than zero.    Ans.: T  
True (T) / False (F)?
3. The relation,  $dG = VdP - SdT$  is valid for a two component system in the solid state.  
T/F?    Ans.: F
4. The reaction,  $\text{CaCO}_3(\text{Solid}) = \text{CaO}(\text{Solid}) + \text{CO}_2(\text{gas})$  was at equilibrium. How many degrees of freedom are there when  $\text{CaO}$  was removed from the system?    Ans.: 2
5. Adsorption has an activation barrier. T/F?    Ans.: T
6. For a second order reaction  $2A \rightarrow \text{products}$ , when  $[A]_0$  is reduced by a factor of 2, the half life doubles. T/F?    Ans.: T
7. Multilayer adsorption is generally physisorption. T/F?    Ans.: T
8. Generally, multiple adsorption sites are expected for dissociative adsorption.  
T/F?    Ans.: T
9. The entropy of activation will always be positive. T/F?    Ans.: F

10. Langmuir adsorption isotherm can be used to find out the surface area of a substrate.  
T/F? Ans.: T
11. For a first order reaction, the amount of the reactant disappears in  $3t_{1/2}$  is \_\_\_\_  
Ans.:  $A_0/8$
12. The overall rate coefficient ( $k_{\text{overall}}$ ) of a composite reaction involving two elementary steps with rate constants,  $k_1$  and  $k_2$ , is given by the expression  $k_{\text{overall}}=k_1/k_2$ . Express the overall activation energy,  $E_{\text{overall}}$  in terms of the activation energies  $E_1$  and  $E_2$  for the elementary steps.  
Ans.:  $E_1-E_2$
13. Steady state approximation is used only when equilibrium is involved between the reactants and the intermediate species. T/F? Ans.: F
14. For a reaction,  $A + B \rightarrow \text{products}$ , if  $[A] \gg [B]$ , the reactant with lower concentration determines the order of the reaction. T/F? Ans.: T
15. There are equations of state applicable to all states of matter. T/F? Ans.: T
16. As the  $\Delta G^\circ$  for a reaction changes from a large negative to a large positive value,  $K$  of the reaction will change from a large positive to a large negative value. T/F?  
Ans.: F
17. The rate of a spontaneous chemical reaction can be affected by removing some products.  
T/F? Ans.: F
18. For a zero order reaction, the plot of rate vs concentration has a positive slope. T/F?  
Ans.: F
-

**PART 2**

Use a separate answer book for questions starting from 19 onwards. Write the following in the answer book:

CY 1001-Module-I (Physical Chemistry)

BATCH: \_\_\_\_\_ ROLL NO: \_\_\_\_\_

NAME: \_\_\_\_\_

---

**Questions from 19 and 20 carry 2 marks each**

19. Supposedly, a supramolecular system (an assembly of molecules) has  $5 \times 10^8$  individual molecules, which can arrange in four different ways. If each arrangement was a random choice of one of these four possibilities, what would be the residual entropy associated with the system?

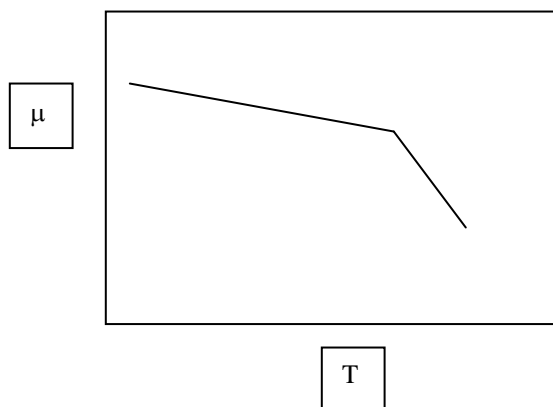
$$S = k \ln \Omega = k \ln 4^{5 \times 10^8} = 5 \times 10^8 k \ln 4 = 9.57 \times 10^{-15} \text{ J / K}$$

20. What is the energy separation at 623 K between the levels in a two level system when the population of the upper state is one half of the lower state?

$$\frac{n_2}{n_1} = e^{-\frac{(\varepsilon_2 - \varepsilon_1)}{kT}} \quad (\varepsilon_2 - \varepsilon_1) = -Tk \ln \frac{n_2}{n_1} = 0.5959 \times 10^{-20} \text{ J}$$

**Questions from 21 to 29 carry 3 marks each**

21. Plot a graph, showing the variation in chemical potential,  $\mu$ , with T for a pure solid undergoing complete sublimation.



22. The rate constant for the decomposition of  $N_2O_5$  ( $N_2O_5 \rightarrow N_2O_4 + 1/2O_2$ ) is  $5.2 \times 10^{-5} \text{ s}^{-1}$  at  $25^\circ\text{C}$  and  $8.2 \times 10^{-3} \text{ s}^{-1}$  at  $75^\circ\text{C}$ . Calculate the activation energy ( $E_a$ ) of the reaction.

$$k_1 = Ae^{[-E_a/RT_1]} \quad (1) \text{ and } k_2 = Ae^{[-E_a/RT_2]} \quad (2)$$

$$(1)/(2) \text{ leads to } \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left\{ \frac{1}{T_2} - \frac{1}{T_1} \right\} \text{ Solve for } E_a. \text{ Ans: } 87.884 \text{ kJ/mol}$$

23. Suppose the transformation of A to B occurs either by:

(i) a reversible first order as:  $(i) A \xrightleftharpoons[k_2]{k_1} B$  or

(ii) a reversible second order reaction involving  $H^+$  ion as in:  $(ii) A + H^+ \xrightleftharpoons[k_4]{k_3} B + H^+$

Express  $k_1$  in terms of  $k_2$ ,  $k_3$  and  $k_4$  when these reactions are at equilibrium.

$k_1[A] = k_2[B]$  hence  $[A] = \frac{k_2[B]}{k_1}$ . Similarly,  $k_3[A][H^+] = k_4[B][H^+]$ . Substitution for A in the

second equilibrium leads to  $k_3 \frac{k_2[B]}{k_1} [H^+] = k_4[B][H^+]$ . Canceling the identical terms on both

sides will lead to the following relation.  $k_1 = \frac{k_2 k_3}{k_4}$

24. The decomposition of  $N_2O_5$ ,  $2N_2O_5 = 4NO_2 + O_2$  is studied by measuring the concentration of oxygen as a function of time. The rate equation found is,

$$\frac{d[O_2]}{dt} = (1.5 \times 10^{-4} \text{ s}^{-1}) [N_2O_5] \text{ at constant temperature and pressure. Under these conditions,}$$

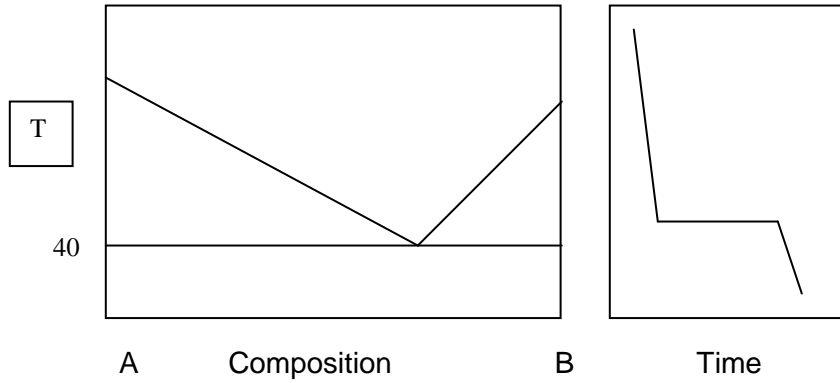
the reaction goes to completion to the right. What is the half life of the reaction under these conditions?

From the rate constant, it is obvious that it is a first order reaction.

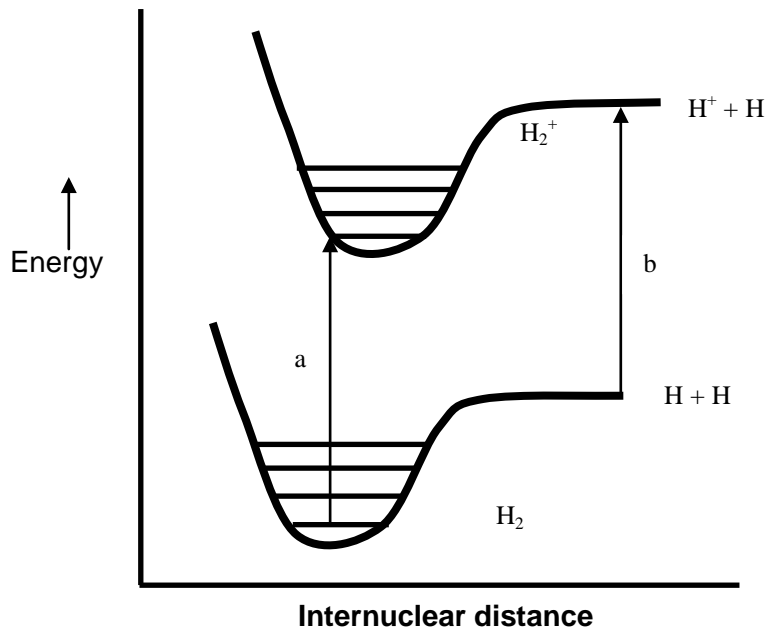
$$\text{Thus, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-4}} = 0.462 \times 10^4 = 4620 \text{ s}$$

However, this equation is valid for A goes to product. Here,  $2N_2O_5$  are decomposing per one  $O_2$  formation. Hence, the  $t_{1/2}$  value becomes  $4620/2 = 2310 \text{ s}$ .

25. A simple eutectic system composed of A and B has a eutectic composition of 40 wt% B and it melts at 40 °C. The melting points of A and B are 100 and 80 °C, respectively. Depict the phase diagram of this system with appropriate labels. Also, draw the cooling curve at the eutectic composition.

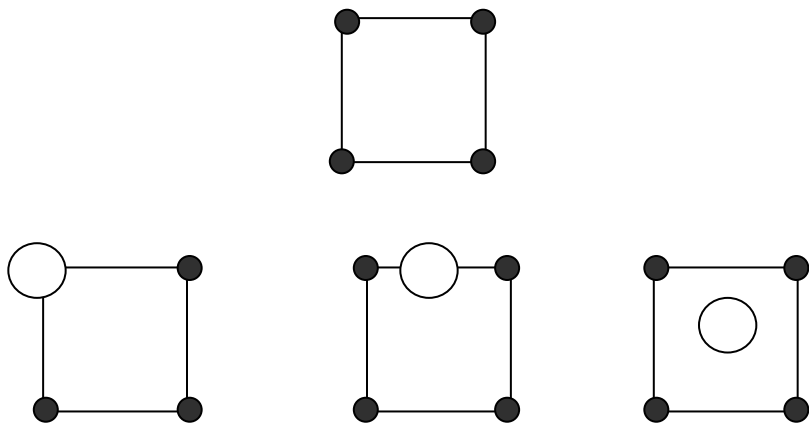


26. In the photoelectron emission process with  $H_2$  involving two electronic energy states, represented schematically below, (a) indicate the lowest ionization energy observed, (b) mark the ionization process of hydrogen atom in this energy level scheme and (c) suggest what the difference between these values correspond to? Draw these curves in your answer book to indicate the answers.

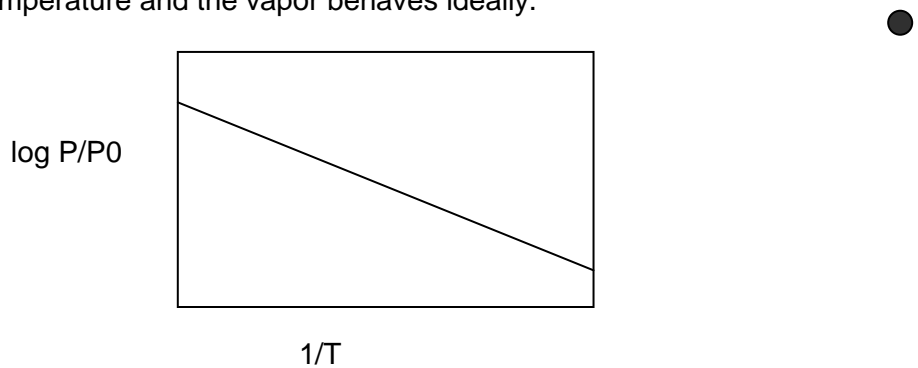


Ans.: c: dissociation energy of the ionic state.

27. Represent the three distinct adsorption geometries of a molecule adsorbed on a surface shown below. Represent the molecule with an open circle, larger than the atoms shown. Only one adsorbed molecule to be shown for a given geometry. You need to reproduce the figure three times and place a molecule at the required site in each figure.



28. Plot a graph in which the vapor pressure of water is plotted against  $1/T$ . Assume that  $\Delta H$  is independent of temperature and the vapor behaves ideally.



29. Calculate the change in boiling point of a liter of water when the pressure above was increased from 1 atm to 10 atm. The heat of vaporization is 539.7 cal/g and volume per gram of the liquid and vapour phases are 1.04 and 1680 ml, respectively at its normal boiling point.

$$\frac{dT}{dP} = ?$$

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_v - V_l)} = ? \text{ atmK}^{-1} \quad \therefore \frac{dT}{dP} = ? \text{ K atm}^{-1}$$

**Questions from 30 to 32 carry 6 marks each**

30. The frequency of vibration of the R-X bond in molecule RX is  $5.0 \times 10^{12} \text{ s}^{-1}$  at 298 K. What is the value of molecular partition function,  $q$ , considering only the first 8 energy levels? (*hint: energy levels are separated by  $h\nu$ , where  $\nu$  is the vibrational frequency*)

We can calculate the partition function by adding the  $e^{-E_i/k_B T}$  terms until the value becomes negligible. The first terms are:

$i$	0	1	2	3.....8
$e^{-E_i / k_B T}$	1	0.447	0.20	0.090.....0.002

The sum of these is 1.8 and is a good approximation to the partition function  $q$ .

31. The equilibrium constant for an association reaction,  $A + B \rightleftharpoons AB$  is  $1.80 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  at 25 °C and  $3.45 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  at 40 °C. Assuming  $\Delta H^0$  to be independent of temperature, calculate  $\Delta H^0$  and  $\Delta S^0$ .

$$\ln K_1 = \frac{-\Delta H}{RT_1} + \frac{\Delta S}{R}$$

$$\ln K_2 = \frac{-\Delta H}{RT_2} + \frac{\Delta S}{R}$$

Thus,

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \text{ Upon substitution, we will get } \Delta H = 33.67 \text{ kJ / mol}; \Delta S = 175.2 \text{ J / Kmol}$$

32. The forward rate constant for the elementary reaction,  $C_2H_6 \rightleftharpoons 2CH_3$  is  $1.57 \times 10^{-3} \text{ s}^{-1}$  at 1000 K. What is the rate constant for the backward reaction at this temperature? For  $CH_3(g)$ ,  $\Delta_f G^\circ = 159.74 \text{ kJ mol}^{-1}$  at 1000 K. For  $C_2H_6$ ,  $\Delta_f G^\circ = 260.76 \text{ kJ mol}^{-1}$  at 1000 K.

$$\Delta_r G^\circ = 2\Delta_f G^\circ(CH_3) - \Delta_f G^\circ(C_2H_6)$$

$$= 2(159.82) - 260.76 = 58.88 \text{ kJ/mol}$$

$$K_p = \exp\left\{\frac{-\Delta_r G^\circ}{RT}\right\}$$

$$= \exp\left\{\frac{-(58.88)}{(8.314 \times 10^{-3})(1000)}\right\} = 9.12 \times 10^{-4}$$

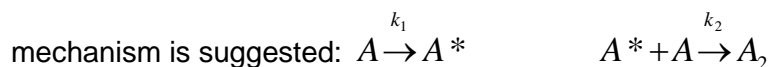
$$K_c = \frac{([CH_3]/c^\circ)^2}{[C_2H_6]/c^\circ} = K_p \frac{P^\circ}{c^\circ RT} = (9.12 \times 10^{-4}) \frac{1 \text{ bar}}{(1 \text{ mol/L})(0.083145)(1000 \text{ K})} = 1.3 \times 10^{-13} \text{ mol/L}$$

$$K_c = \frac{k_f}{k_b}$$

$$k_b = \frac{k_f}{K_c} = \frac{1.57 \times 10^{-3}}{1.3 \times 10^{-13}} = 1.23 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

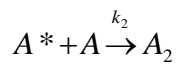
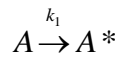
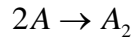
**Question 33 carries 8 marks**

33. A dimerization  $2A \rightarrow A_2$  is found to be first order, with a half life of 666 s. The following



where  $k_2 \gg k_1$ . (a) What is the value for the rate constant  $k_1$ ? (b) What is the rate law representing the overall reaction? (c) If the initial concentration of A is 0.05 M, how much time is required to reach  $[A] = 0.0125 \text{ M}$ ?





$$(a) t_{1/2} = 666 = \frac{0.693}{k} \Rightarrow k = 1.04 \times 10^{-3} \text{ s}^{-1}$$

but  $k_1 = \frac{k}{2} \Rightarrow k_1 = 5.20 \times 10^{-4} \text{ s}^{-1}$  ( $k$  is the overall rate constant. they have to work out question (b) to find this relation)

(b) Applying steady state approximation

$$\frac{dA^*}{dt} = 0 = k_1[A] - k_2[A^*][A]$$

$$k_2[A^*] = k_1$$

$$[A^*] = \frac{k_1}{k_2}$$

$$\text{rate} = \frac{1}{2} \frac{d[A]}{dt} = k_2[A^*][A] = k_1[A]$$

$$\text{rate} = 2k_1[A] = k[A] \quad \left\{ \Rightarrow k_1 = \frac{k}{2} \right\}$$

$$(c) \ln \frac{[A]_0}{[A]} = kt$$

$$\ln \frac{0.05}{0.0125} = 1.04 \times 10^{-3} t$$

$$\Rightarrow t = \frac{1.38}{1.04 \times 10^{-3}} = 1.33 \times 10^3 \text{ s}$$